FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: **219924US2PCT**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): 10/088089

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/03209	**17 NOVEMBER 2000**	**17 NOVEMBER 1999**

TITLE OF INVENTION

TRANSPARENT SUBSTRATE COMPRISING AN ANTIREFLECTION COATING

APPLICANT(S) FOR DO/EO/US

Laurent JORET, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority / PCT/IB/308 / PT0-1449
Drawing (1 sheet)
Petition To Revive

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/088089	PCT/FR00/03209	219924US2PCT

24. The following fees are submitted:.	CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$130.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	22 - 20 =	2	x $18.00	**$36.00**	
Independent claims	1 - 3 =	0	x $84.00	**$0.00**	
Multiple Dependent Claims **(check if applicable)**.			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**$1,056.00**	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				**$0.00**	
SUBTOTAL =				**$1,056.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$130.00**	
TOTAL NATIONAL FEE =				**$1,186.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐				**$0.00**	
TOTAL FEES ENCLOSED =				**$2,466.00**	
TOTAL FEE INCLUDES PETITION TO REVIVE FEE OF $1,280.00				**Amount to be: refunded**	$
				charged	$

a. ☒ A check in the amount of **$2,466.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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REGISTRATION NUMBER

March 21 2002
DATE

DOCKET NO. 219924US2PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: Laurent JORET, et al.

SERIAL NO: NEW U.S. PCT APPLICATION: Based on PCT/FR00/3209

FILED: HEREWITH : 17 NOVEMBER 2000

FOR: TRANSPARENT SUBSTRATE COMPRISING AN ANTIREFLECTION COATING

PETITION TO REVIVE UNDER 37 C.F.R. 1.137(b)

ASSISTANT COMMISSIONER OF PATENTS & TRADEMARKS
WASHINGTON, D.C. 20231

SIR:

Applicants respectfully petition that the present application be revived under 37 CFR 1.137(b).

The national stage under 35 U.S.C. 371 of the above-identified International PCT application was due to be entered in the United States as a designated office by 17 JULY 2001. However, due to an unintentional and inadvertent error, the application was not timely filed. Applicants state that the entire delay in filing the required reply from the due date for the reply until the filing of a grantable petition pursuant to 37 CFR 1.137(b) was unintentional.

Accompanying this petition is a complete application under 35 U.S.C. 371 including payment of the appropriate basic national fee, and an English translation of the International PCT application.

A check in the amount of $2,466.00 is being submitted herewith to cover the required petition fee.

Applicants therefore believe that the present application is in proper condition to be revived and restored to a pending status. An early and favorable decision is hereby earnestly solicited.

Respectfully submitted,

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APPLICATION DATA SHEET

APPLICATION INFORMATION

Application Number::	10/088,089
Application Date::	03/21/02
Application Type::	REGULAR
Subject Matter::	UTILITY
CD-ROM or CD-R?::	NONE
Title::	TRANSPARENT SUBSTRATE COMPRISING AN ANTIGLARE COATING
Attorney Docket Number::	219924US2PCT

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CORRESPONDENCE INFORMATION

Correspondence Customer Number:: 22850

REPRESENTATIVE INFORMATION

Representative Customer Number:: 22850

DOMESTIC PRIORITY INFORMATION

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	National Stage of	PCT/FR00/03209	11/17/00

FOREIGN PRIORITY INFORMATION

Application Number:	Country::	Filing Date::	Priority Claimed::
99/14423	France	11/17/99	YES

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219924US-2 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

LAURENT JORET ET AL. : ATTN: APPLICATION DIVISION

SERIAL NO: NEW U.S. PCT APPLN :
(BASED ON PCT/FR00/03209)

FILED: HEREWITH :

FOR: TRANSPARENT SUBSTRATE COMPRISING AN ANTIREFLECTION COATING

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to a first examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please cancel Claim 1-22 without prejudice.

Please add new Claims 23-44 as follows:

23. (New) Transparent substrate, comprising:

on at least one face of the transparent substrate, an antireflection coating, made of a stack of thin layers of dielectric material having alternately high and low refractive indices, wherein the stack comprises, in succession:

a high-index first layer, having a refractive index n_1 of between 1.8 and 2.2 and a geometrical thickness e_1 of between 5 and 50 nm;

a low-index second layer, having a refractive index n_2 of between 1.35 and 1.65 and a geometrical thickness e_2 of between 5 and 50 nm;

a high-index third layer, having a refractive index n_3 of between 1.8 and 2.2 and a geometrical thickness e_3 of between 70 and 120 nm;

a low-index fourth layer, having a refractive index n_4 of between 1.35 and 1.65 and a geometrical thickness e_4 of at least 80 nm.

24. (New) Substrate according to Claim 23, wherein n_1 and/or n_3 are between 1.85 and 2.15, especially between 1.90 and 2.10.

25. (New) Substrate according to Claim 23, wherein n_2 and/or n_4 are between 1.35 and 1.55.

26. (New) Substrate according to Claim 23, wherein e_1 is between 5 and 50 nm, especially between 10 and 30 nm or between 15 and 25 nm.

27. (New) Substrate according to Claim 23, wherein e_2 is between 5 and 50 nm, especially between 10 and 35 nm and preferably less than or equal to 30 nm.

28. (New) Substrate according to Claim 23, wherein e_3 is less than or equal to 120 nm and especially at least 75 Nm.

29. (New) Substrate according to Claim 23, wherein e_4 is greater than or equal to 80 nm and especially less than or equal to 120 nm.

30. (New) Substrate according to Claim 23, wherein the high-index first layer and the low-index second layer are replaced with a single layer having an intermediate index e_5 of

between 1.65 and 1.80 and preferably having an optical thickness e_{opt5} of between 50 and 140 nm, preferably between 85 and 120 nm.

31. (New) Substrate according to claim 30, wherein the intermediate-index layer is based on a mixture of silicon oxide and at least one metal oxide chosen from tin oxide, zinc oxide and titanium oxide, or is based on a silicon oxynitride or oxycarbide and/or on aluminium oxynitride.

32. (New) Substrate according to Claim 23, wherein the high-index first layer and/or the high-index third layer are based on one or more metal oxides chosen from zinc oxide, tin oxide, and zirconium oxide, or based on one or more nitrides chosen from silicon nitride and aluminium nitride.

33. (New) Substrate according to Claim 23, wherein the high-index first layer and/or the high-index third layer include a superposition of several high-index layers, especially a superposition of two layers such as SnO_2/Si_3N_4 or Si_3N_4/SnO_2.

34. (New) Substrate according to Claim 23, wherein the low-index second layer and/or the low-index fourth layer are based on silicon oxide, silicon oxynitride and/or oxycarbide, or on a mixed silicon aluminium oxide.

35. (New) Substrate according to Claim 23, wherein the substrate is made of clear or bulk-tinted glass.

36. (New) Substrate according to Claim 23, wherein light reflection on a side where the stack of thin layers is provided is reduced by a minimum value of 3 or 4% at an angle of incidence of between 50° and 70°.

37. (New) Substrate according to Claim 23, wherein a colorimetric response of light reflection on a side where the stack of thin layers is provided is such that corresponding a*

and b* values in the (L*, a*, b*) colorimetry system are negative at an angle of incidence of between 50° and 70°.

38. (New) Substrate according to Claim 23, wherein the antireflection stack uses, at least for its high-index third layer, silicon nitride or aluminium nitride to undergo a heat treatment of bending, toughening, or annealing.

39. (New) Glazing according to Claim 23, wherein it is composed of the single substrate provided, on one of its faces, with the multilayer antireflection stack and, on its other face, either with no antireflection stack or also with a multilayer antireflection stack, or with another type of antireflection coating, or with a coating having another functionality of solar-protection, low-emissivity, antifouling, antifogging, anti-rain, or heating.

40. (New) Glazing according to Claim 23, wherein it has a laminated structure in which two glass substrates are joined together using a sheet of thermoplastic, the substrate being provided, on the opposite side to the join, with the antireflection stack and the substrate being provided, on the opposite side to the join, either with no antireflection coating, or also with an antireflection stack, or with another type of antireflection coating, or with a coating having another functionality of the solar-protection, low-emissivity, antifouling, antifogging, anti-rain, or heating, the coating having another functionality possibly also being on one of the faces of the substrates which are turned towards the thermoplastic joining sheet.

41. (New) Glazing according to Claim 23, wherein it has a laminated structure with one or more sheets of joining polymer, with the antireflection coating on at least one of the 1 and 4 faces and, in contact with the joining sheet or one of the joining sheets, a solar-protection coating, especially one including two silver layers.

42. (New) Glazing according to Claim 39, wherein the other type of antireflection coating is chosen from the following coatings:

a single low-index layer, having an index of less than 1.60 or 1.50, especially about 1.35-1.48, especially based on silicon oxide;

a single layer whose refractive index varies through its thickness, especially of the silicon oxynitride SiO_xN_y type, where x and y vary through its thickness;

a two-layer stack, comprising, in succession, a layer having a high index of at least 1.8, especially made of tin oxide, zinc oxide, zirconium oxide, titanium oxide, silicon nitride or aluminium nitride, and then a layer having a low index, of less than 1.65, especially made of silicon oxide, oxynitride, or oxycarbide;

a three-layer stack comprising, in succession, a layer having a medium index of between 1.65 and 1.8 of the silicon oxycarbide or oxynitride and/or aluminium oxycarbide or oxynitride type, a layer having a high index of greater than 1.9 of the SnO_2 or TiO_2 type, and a layer having a low index of less than 1.65, of the mixed Si-Al oxide or silicon oxide type.

43. (New) Process for obtaining the glazing according to Claim 39, wherein the antireflection stack or stacks are deposited by sputtering and the optional antireflection coating is deposited by a sol-gel technique, by a pyrolysis technique of CVD or plasma CVD, by sputtering, or by corona discharge.

44. (New) Application of the glazing according to Claim 39 as interior or exterior glazing for buildings, as a shop display cabinet or counter, which may be curved, as glazing for a vehicle side window, for a vehicle rear window, for a vehicle sunroof, for a vehicle windscreen, or as glazing for protecting objects of the painting, or as an antidazzle computer screen, or as glass furniture.

IN THE ABSTRACT

Please cancel the Abstract on page 32 in its entirety and insert therefor:

ABSTRACT

A transparent substrate including an antireflection coating, made from a stack of thin layers of dielectric material having alternately high and low refractive indices. This stack includes a high-index first layer having a refractive index n_1 of between 1.8 and 2.2 and a geometrical thickness e_1 of between 5 and 50 nm, a low-index second layer having a refractive index n_2 of between 1.35 and 1.65 and a geometrical thickness e_2 of between 5 and 50 nm, a high-index third layer having a refractive index n_3 of between 1.8 and 2.2 and a geometrical thickness e_3 of between 70 and 120 nm, and a low-index fourth layer having a refractive index n_4 of between 1.35 and 1:65 and a geometrical thickness e_4 of at least 80 nm.

REMARKS

Favorable consideration of this application, as presently amended, is respectfully requested.

The present response is submitted to place the above-identified application in more proper format under United States practice.

By the present preliminary amendment original Claims 1-22 are canceled and new Claims 23-44 are presented for examination. New Claims 23-44 are similar to original Claims 1-22 except that new Claims 23-44 do not recite any reference numerals or improper multiple dependencies, and correct for minor informalities in original Claims 1-22.

A new Abstract believed to be in more proper format under United States practice is also submitted herein.

The present application is believed to be in condition for a full and thorough examination on the merits. An early and favorable consideration of the present application is hereby respectfully requested.

Respectfully submitted,

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219924US-2 PCT

Marked-Up Copy
Serial No: _____
Amendment Filed on:
3-21-2002

IN THE CLAIMS

--Claim 1-22 (Canceled).

Claims 23-44 (New).

IN THE ABSTRACT

(New).--

1/pats

TRANSPARENT SUBSTRATE COMPRISING AN ANTIREFLECTION COATING

The invention relates to a transparent substrate, especially made of glass, intended to be incorporated into glazing and provided, on at least one of its faces, with an antireflection coating.

An antireflection coating usually consists of a stack of interferential thin layers, generally an alternation of layers based on a dielectric material having high and low refractive indices. The purpose of such a coating, deposited on a transparent substrate, is to reduce its light reflection, and therefore to increase its light transmission. A substrate coated in this way therefore has its transmitted light/reflected light ratio increased, thereby improving the visibility of objects placed behind it. When it is desired to achieve the maximum antireflection effect, it is then preferable to provide both faces of the substrate with this type of coating.

There are many applications of this type of product: it may serve for glazing in buildings, for example as a shop display cabinet and as architectural curved glass, so as to more clearly distinguish what is displayed in the window, even when the internal lighting is low compared with the external lighting. It may also serve as glass for a counter.

An application in the fitting-out of vehicles has also been envisaged, especially for cars and trains. Giving a windscreen an antireflection effect is particularly advantageous on several counts: it can increase the light transmission into the passenger compartment, and therefore increase the visual comfort of the passengers. It also makes it possible to eliminate the undesirable reflections which annoy the driver, particularly reflections of the dashboard.

Examples of antireflection coatings are described in patents EP 0 728 712 and WO 97/43224.

However, whether referring to display cabinets, counter glass or windscreens, the glazing involved, once fitted, is not necessarily in a vertical position unlike conventional glazing in buildings, for example curtain walling. Windscreens are usually inclined at about 60°, while shop windows and counters are often curved with variable angles of observation.

Now, most antireflection coatings developed hitherto have been optimized to minimize light reflection at normal incidence, without taking into account the optical appearance of the glazing viewed obliquely. Thus, it is known that at normal incidence it is possible to obtain very low light reflection values R_L with stacks consisting of four layers with a high-index layer/low-index layer/high-index layer/low-index layer alternation. The high-index layers are generally made of TiO_2, which actually has a very high index of about 2.45, and the low-index layers are usually made of SiO_2. The optical thicknesses of the layers (their geometrical thickness multiplied by their refractive index) are expressed successively in the following manner: (e1 + e2) < □/4 - e3 ≥ λ/2 - e4 = λ/4, where λ is the wavelength averaged over the visible range around 500 nm and e1 to e4 are the thicknesses of the four layers deposited in succession on the substrate. The coating may also comprise a three-layer stack. In this case, it is preferable that the optical thicknesses e'1, e'2 and e'3 of the layers in the order in which they are deposited on the substrate satisfy the following conditions: □/4 - □/2 - □/4.

However, the appearance in reflection, especially the intensity of the light reflection, is not satisfactory when the viewing angle moves slightly away from perpendicular to the glazing.

Studies have been conducted in order to take into account an oblique viewing angle, but these have not been completely satisfactory either: mention may be made, for example, of patent EP-0 515 847 which

proposes a two-layer stack of the TiO_2+SiO_2/SiO_2 type or a three-layer stack of the $TiO_2+SiO_2/TiO_2/SiO_2$ type deposited by sol-gel, but this stack is not as efficient.

The object of the invention is therefore to remedy the abovementioned drawbacks, by seeking to develop an antireflection coating which can reduce the level of light reflection from a transparent substrate of the glass type over a wider angle-of-incidence range, and more particularly at an oblique angle of incidence ranging from 50 to 70° with respect to the vertical, and this being achieved without compromising the economic and/or industrial feasibility of its manufacture. Secondarily, the subject of the invention is the development of such a coating which is furthermore capable of withstanding heat treatments, especially if the carrier substrate is a glass which, in its final application, must be annealed, bent or toughened.

The subject of the invention is first of all a transparent substrate, especially made of glass, comprising, on at least one of its faces, an antireflection coating consisting of thin layers of dielectric material having alternately high and low refractive indices, especially creating an antireflection effect at oblique incidence, the said substrate being defined as follows. It comprises, in succession:

→ a high-index first layer 1, having a refractive index n_1 of between 1.8 and 2.2 and having a geometrical thickness e_1 of between 5 and 50 nm;

→ a low-index second layer 2, having a refractive index n_2 of between 1.35 and 1.65 and a geometrical thickness e_2 of between 5 and 50 nm;

→ a high-index third layer 3, having a refractive index n_3 of between 1.8 and 2.2 and a geometrical thickness e_3 of between 70 and 120 nm;

→ a low-index fourth layer 4, having a refractive index n_4 of between 1.35 and 1.65 and a geometrical thickness e_4 of at least 80 nm.

Within the meaning of the invention, the term "layer" is understood to mean either a single layer or a superposition of layers in which each of them complies with the refractive index indicated and in which the sum of their geometrical thicknesses again remains equal to the value indicated for the layer in question.

Within the meaning of the invention, the layers are made of a dielectric material, especially of the oxide or nitride type, as will be explained in detail below. However, this does not exclude at least one of them being modified so as to be at least slightly conducting, for example by doping it with a metal oxide, so as, for example, to also give the antireflection stack an antistatic function.

The invention preferably applies to glass substrates, but it also applies to transparent substrates based on a polymer, for example polycarbonate.

The invention therefore relates to an antireflection stack of the four-layer type. This is a good compromise as the number of layers is large enough for their interferential interaction to make it possible to achieve a large antireflection effect. However, this number remains sufficiently reasonable for the product to be able to be manufactured on a large scale, on an industrial line, on large substrates.

The thickness and refractive-index criteria adopted in the invention make it possible to obtain an antireflection effect over a broad band of low light reflection, even at high angles of incidence such as 50 to 70°, something which is exceptional (this does not prevent, of course, the antireflection stacks of the invention from also reducing the light reflection at normal incidence).

It has proved difficult to select these criteria, since the inventors have taken into account the industrial feasibility of the product and the appearance in light reflection at two levels: both wishing to minimize the value of the light reflection R_L at oblique incidence itself but also wishing to obtain, for this oblique light reflection, a satisfactory colorimetric response, that is to say a colour in reflection whose tint and intensity are acceptable from the aesthetic standpoint.

The inventors have succeeded in this, especially by lowering the value of R_L by at least 3 or 4% between 50° and 70° under illuminant D_{65}, and preferably obtaining negative values of a* and b* in the (L, a*, b*) colorimetry system for this same light reflection. This results in a significant reduction in reflections and a colour in the blue-greens in reflection, which is currently judged to be aesthetically attractive in many applications, especially in the automobile industry.

Perhaps the two most striking characteristics of the invention are the following:

→ firstly, compared with a standard four-layer antireflection coating, the thickness of the last, low-index, layer has been significantly increased: its preferred thickness is greater than the value of $\lambda 4$ normally used;

→ secondly, it has been discovered that, unlike the choice usually made for the high-index layers, it was unnecessary, and even disadvantageous, to choose materials having a very high index, such as TiO_2. On the contrary, for these layers it has proved more judicious to use materials having a more moderate refractive index, especially of at most 2.2. This therefore goes counter to the known teaching on antireflection stacks in general.

The inventors have thus exploited the fact that, at oblique incidence, the low-reflection spectrum broadens and that it is thus possible to be able to use

materials whose index is around 2, such as tin oxide SnO_2 or silicon nitride Si_3N_4. Especially as compared with TiO_2, these materials have the advantage of being able to be deposited at much higher rates when the deposition technique called sputtering is used. Within this moderate range of indices, there is also a greater choice of materials that can be deposited by sputtering, which offers greater flexibility in industrial manufacture and more options for adding further functionalities to the stack, as will be explained in detail below.

These "moderate"-index materials also offer greater flexibility from the strictly optical standpoint: it has been discovered that they allow finer adjustment of the "pair" of values defining most specifically the light reflection (layer side) from the substrate, namely on the one hand the light reflection value R_L and, on the other hand, the a* and b* values corresponding to it at oblique incidence (as will become apparent from the detailed examples below; it is in fact possible to favour one or other of these two values depending on the intended objective or application more).

They also enable the stack to be made overall optically less sensitive, especially from the colorimetric standpoint, to the thickness variations of the layers in the stack and to the variations in the angles of incidence at which the glasses are observed.

Given below are the preferred ranges of the geometrical thicknesses and of the indices of the four layers of the stack according to the invention:

→ for the first and/or third layer, those with a high index:

- n_1 and/or n_3 are advantageously between 1.85 and 2.15, especially between 1.90 and 2.10,
- e_1 is advantageously between 5 and 50 nm, especially between 10 and 30 nm or between 15 and 25 nm,

- e_3 is advantageously less than or equal to 120 nm or less than or equal to 110 nm, and is especially at least 75 nm;

→ the second and/or fourth layer, those with a low index:

- n_2 and/or n_4 are advantageously between 1.35 (or 1.40) and 1.55,

- e_2 is advantageously between 5 and 50 nm, and is especially less than or equal to 35nm or less than or equal to 30 nm, especially being between 10 and 35 nm,

- e_4 is advantageously greater than or equal to 90 or 80 nm, and is especially less than or equal to 120 or 110 nm.

According to an alternative embodiment of the invention, the high-index first layer 1 and the low-index second layer 2 may be replaced with a single layer 5 having a so-called "intermediate" refractive index n_5, especially one between 1.65 and 1.80, and preferably having an optical thickness $e_{opt.5}$ of between 50 and 140 nm (preferably from 85 to 120 nm). In conventional three-layer antireflection stacks, optimized for perpendicular viewing, this thickness is somewhat above 120 nm. This intermediate-index layer has an optical effect similar to that of a high-index layer/low-index layer sequence when it forms the first sequence, i.e. the two layers closest to the substrate bearing the stack. It has the advantage of reducing the overall number of layers in the stack. It is preferably based on a mixture of, on the one hand, silicon oxide and, on the other hand, at least one metal oxide chosen from tin oxide, zinc oxide and titanium oxide. It may also be based on silicon oxynitride or oxycarbide and/or based on aluminium oxynitride.

The materials most suitable for forming the first and/or the third layer, those having a high index, are based on one or more metal oxides chosen from zinc oxide ZnO, tin oxide SnO_2 and zirconium oxide ZrO_2. They may also be based on one or more nitrides

chosen from silicon nitride Si_3N_4 and aluminium nitride AlN.

Using a nitride layer for one or other of the high-index layers, especially the third layer at least, makes it possible to add a functionality to the stack, namely an ability to better withstand the heat treatments without any appreciable impairment in its optical properties. Now, such a functionality is important in the case of glazing of the windscreen or shop counter type, since the glazing has to undergo high-temperature heat treatments of the bending, toughening, annealing or laminating type, in which the glasses have to be heated to at least 120°C (for laminating) up to 500 to 700°C (for bending and toughening). It then becomes paramount to be able to deposit the thin layers before the heat treatment without this causing a problem (to deposit layers on bent glass is tricky and expensive, and it is much simpler from the industrial standpoint to carry out the deposition before any heat treatment).

It is thus possible to have a single configuration of antireflection stack whether or not the carrier glass is intended to undergo a heat treatment.

Even if it is not intended to be heated, it is still beneficial to use at least one nitride layer as this improves the mechanical and chemical durability of the stack in its entirety.

According to one particular embodiment, the first and/or third layer, those having a high index, may in fact be formed from several superposed high-index layers. Most particularly, they may form a bilayer of the SnO_2/Si_3N_4 or Si_3N_4/SnO_2 type. This has the following advantage: the Si_3N_4 tends to be deposited a little less easily and a little more slowly by reactive sputtering than a conventional metal oxide such as SnO_2, ZnO or ZrO_2. Especially for the third layer, which is the thickest and most important for protecting the stack from any damage resulting from a

heat treatment, it may be beneficial to duplicate the layer so as to just bring the Si_3N_4 thickness sufficient to obtain the effect of protection against the desired heat treatments and to optically "supplement" the layer with SnO_2 or ZnO.

The most appropriate materials for forming the second and/or the fourth layer, those having a low index, are based on silicon oxide, silicon oxynitride and/or oxycarbide or else based on a mixed silicon aluminium oxide. Such a mixed oxide tends to have better durability, especially chemical durability, than pure SiO_2 (an example of this is given in patent EP-791 562). The respective proportions of the two oxides may be adjusted in order to improve the expected durability without excessively increasing the refractive index of the layer.

The glass chosen for the substrate coated with the stack according to the invention or for the other substrates which are associated with it in order to form a glazing assembly, may in particular be, for example, extra clear of the "Diamant" type or clear of the "Planilux" type or tinted glass of the "Parsol" type, these three products being sold by Saint-Gobain Vitrage, or else may be of the "TSA" or "TSA ++" type as described in patent EP 616 883. It may also be an optionally tinted glass as described in patents WO 94/14716, WO 96/00194, EP 0 644 164 or WO 96/28394. It may act as a filter against ultraviolet-type radiation.

The substrate or substrates may have undergone heat treatments, that the antireflection stack according to the invention is capable of withstanding, such as annealing, toughening, bending or even folding, that is to say bending with a very small radius of curvature (application in particular for shop counters and windows), most particularly when at least the high-index third layer of the stack contains silicon nitride or aluminium nitride. This means that such heat treatments have no or virtually no effect on the

mechanical and chemical durability of the stack and do not modify (or only very slightly modify) its optical properties.

The subject of the invention is also glazing incorporating the substrates provided with the multilayer stack defined above. The glazing in question may be "monolithic", that is to say composed of a single substrate coated with the multilayer stack on one of its faces. Its opposite face may be devoid of any antireflection coating, being bare or covered with a coating having another functionality. This may be a coating having a solar-protection function (using, for example, one or more silver layers surrounded by dielectric layers, or layers of nitrides such as TiN or ZrN or of metal oxides or of steel or of an Ni-Cr alloy), having a low-emissivity function (for example one made of a doped metal oxide, such as F:SnO_2 or tin-doped indium oxide ITO or one or more silver layers), having an antistatic function (an oxygen-substoichiometric or doped metal oxide), a heating layer (a Cu- or Ag-doped metal oxide, for example) or an array of heating wires (copper wires or bands screen-printed using a conducting silver paste), an antifogging function (using a hydrophilic layer), an anti-rain function (using a hydrophobic layer, for example one based on a fluoropolymer) or an antifouling function (a photocatalytic coating comprising at least partially crystallized TiO_2 in the anatase form).

The said opposite face may also be provided with an antireflection stack to maximize the desired antireflection effect. In this case, this may also be an antireflection stack meeting the criteria of the present invention or it may be another type (B) of antireflection coating.

One particularly beneficial glazing assembly incorporating a substrate coated according to the invention has a laminated structure, which consists of two glass substrates joined together by one or more sheets of a thermoplastic such as polyvinyl butyral

PVB. In this case, one of the two substrates is provided, on the external face (the face opposite that where the glass joins the thermoplastic sheet), with the antireflection stack (A) according to the invention. The other glass, also on its external face, may, as previously, be bare, coated with layers having another functionality, coated with the same antireflection stack (A) or with another type (B) of antireflection stack, or else with a coating having another functionality as in the previous case (this other coating may also be placed not on a face opposite the join but on one of the faces of one of the rigid substrates which points towards the side with the thermoplastic joining sheet). Conventionally, the faces of the glazing are numbered starting from the outermost face. Thus, it is possible to have the antireflection stack according to the invention on the 1 and/or 4 faces (that is to say on the face of the glass panes pointing towards the outside of the glazing, when there are two glass panes).

It is therefore possible to provide the laminated glazing with an array of heating wires, with a heating layer or with a solar-protection coating on the "inside" of the laminate (and therefore on the 2 and/or 3 faces). Solar-protection coatings based on two silver layers sandwiched between three layers or multilayers made of particularly appropriate dielectric material are described in patents EP 638 528, EP 718 250, EP 844 219 and EP 847 965.

According to another alternative embodiment, instead of depositing the solar-protection coating on one of the rigid substrates (one of the glass panes), it is possible to deposit it on a sheet of polymer of the PET (polyethylene terephthalate) type, which is placed between two sheets of thermoplastic polymer of the PVB type before being laminated with the two glass panes. This type of configuration is especially described in patents EP 758 583, US 5 932 329, EP 839 644, WO 99/45415 and EP 1 010 677.

An antifouling layer (for example based on photocatalytic TiO_2 as described in patents WO 97/10186, WO 97/10185 or WO 99/44954), or else a hydrophilic or hydrophobic layer may be placed on the "outside" (and therefore on the 1 or 4 faces, on the face not covered with the antireflection stack according to the invention).

It is thus possible to have configurations of the type:

antireflection coating (A)/glass/PVB/bare or anti-fouling, hydrophilic or hydrophobic functionalized glass;

antireflection coating (A)/glass/PVB/glass/ antireflection coating (A) or (B);

antireflection coating (A)/glass/PVB/PET provided on one of its faces with a solar-protection coating/ PVB/glass/optional antireflection coating (A) or (B);

antireflection coating (A)/glass/PVB/solar-protection coating/glass/optional antireflection coating (A) or (B);

antireflection coating (A)/glass/solar-protection coating/PVB/glass/optional antireflection coating (A) or (B).

These configurations, especially with both substrates bent and/or toughened, make it possible to obtain motor-vehicle glazing, and especially a highly advantageous windscreen since the standards impose, on motor vehicles, windscreens with a high light transmission, of at least 75% at normal incidence according to the European standards. By incorporating antireflection coatings in the usual windscreen laminated structure, the light transmission of the glazing is increased, for example by at least 6%, this being advantageous as it allows more light into the passenger compartment of the vehicle, providing better comfort and safety. In another use, the reduction in light reflection may serve to reduce the energy transmission while still complying with the standards in terms of light transmission. Thus, it is possible to

increase the solar-protection effect of the windscreen, for example by absorption in the glass substrates, using glass substrates that are tinted more strongly. Specifically, it is thus possible to make the light reflection value of a standard laminated windscreen go from 13.6% to less than 6.5%, while still reducing its energy transmission by at least 7%, taking it for example from 48.5% to 41.5%, with a constant light transmission of 75%.

Various objectives may be achieved by choosing another antireflection coating, of the (B) type, for the other face of the glazing (whether this is monolithic or laminated). It may be desirable for the second coating to be even simpler to manufacture and for it therefore to have a smaller number of layers. It may also be beneficial to differentiate the required level of durability for the two coatings according to their degree of exposure to mechanical or chemical assault. Thus, for glazing fitted into a vehicle, it may be judicious to provide the external face of the glazing with a more durable coating, even if optically it is less efficient, than the inner face turned towards the passenger compartment (the reader need only think, for example, of the repeated mechanical assault by the windscreen wiper blades).

The invention also includes glazing provided with the antireflection stack of the invention and in the form of multiple glazing, that is to say using at least two substrates separated by an intermediate gas-filled cavity (double or triple glazing). Here again, the other faces of the glazing may also be antireflection-treated or may have another functionality.

It should be noted that this other functionality may also consist in placing, on the same face, the antireflection stack and the stack having another functionality (for example by surmounting the antireflection coating with a very thin antifouling coating layer).

Greater durability may be obtained by reducing the number of layers, or even keeping only one of them, in order to minimize the internal stresses in the stack and the risks of delamination, and/or by tailoring the process of depositing the layers. It is known that hot deposition, using pyrolysis techniques for example, make it possible to obtain layers that are more adherent and stronger than those deposited cold, for example by sputtering.

This type-B antireflection coating may be chosen from one of the following coatings:

→ a single low-index layer, having a refractive index of less than 1.60 or 1.50, especially about 1.35 to 1.48. It is preferably an SiO_2 layer having a thickness of between 80 and 120 nm, which may be deposited by sol-gel, CVD, corona discharge or sputtering;

→ again only a single layer, but one whose refractive index varies through its thickness in order to improve the performance thereof. It may especially be a layer based on silicon oxynitride SiO_xN_y, where x and y vary through its thickness, or based on a mixed silicon titanium oxide $Si_zTi_{1-z}O_2$, where z varies through the thickness of the layer. This type of coating may be deposited by plasma CVD and is explained in detail in patent FR 98/16118 of 21 December 1998;

→ a two-layer stack comprising, in succession, a layer having a high index of at least 1.8 (especially made of tin oxide SnO_2, zinc oxide ZnO, zirconium oxide ZrO_2, titanium oxide TiO_2, silicon nitride Si_3N_4 and/or aluminium nitride AlN) and then a layer having a low index of less than 1.65, especially made of silicon oxide, oxynitride or oxycarbide;

→ a three-layer stack comprising, in succession, a layer of medium index between 1.65 and 1.80, of the silicon oxycarbide or oxynitride and/or aluminium oxycarbide or oxynitride type, a layer having an index equal to or greater than 1.9, such as SnO_2, ZnO, ZrO_2, Si_3N_4 or TiO_2, and again a layer having a low index of

less than 1.65, made of SiO_2 or a mixed silicon aluminium oxide (possibly fluorinated according to the aforementioned patent EP-791 562), as may be all the other mixed Si-Al oxide layers mentioned above).

The subject of the invention is also the process for manufacturing the glass substrates with an antireflection coating (A) according to the invention. A process consists in depositing all the layers, in succession, one after the other, by a vacuum technique, especially by magnetic-field-enhanced sputtering or by corona discharge. Thus, it is possible to deposit the oxide layers by reactive sputtering of the metal in question in the presence of oxygen and the nitride layers in the presence of nitrogen. To make SiO_2 or Si_3N_4, the process can start with a silicon target which is lightly doped with a metal such as aluminium in order to make it sufficiently conducting.

In the case of the optional antireflection coating B of another type, several deposition techniques are possible, those involving a heat treatment or those carried out cold, especially the sol-gel technique, pyrolysis techniques carried out in the pulverulent, solid or vapour phase, the latter also being known by the name CVD (Chemical Vapour Deposition). The CVD may be plasma-enhanced CVD. It is also possible to use vacuum techniques of the sputtering type.

The antireflection coating A may also be deposited hot. Preferably, the coating A is deposited by sputtering and the coating B by pyrolysis of the CVD type. It is also possible, as recommended by the aforementioned patent WO 97/43224, for some of the layers of one or other of the stacks to be deposited by a hot deposition technique of the CVD type, the rest of the stack being deposited cold by sputtering.

The subject of the invention is also applications of such glazing, most of which have already been mentioned: shop windows, display cabinets and counters, glazing for buildings, glazing for any

land-, air- or sea-going vehicle, especially the windscreen of a vehicle, the rear window, sunroof, side windows or antidazzle screens, for any display device such as computer screens, televisions, any glass furniture or any decorative glass. Such glazing may be bent/toughened after the layers have been deposited.

The details and advantageous characteristics of the invention will now be apparent from the following non-limiting examples, with the aid of the figures:

- **Figure 1**: a substrate provided with a four-layer antireflection stack A according to the invention;
- **Figure 2**: monolithic glazing provided with two antireflection stacks (A, A) or (A, B);
- **Figure 3**: laminated glazing provided with two antireflection stacks (A, A) or (A, B).

Figure 1, which is highly schematic, shows in cross section a glass pane 6 surmounted by a four-layer antireflection stack (A).

Figure 2, also highly schematic, shows monolithic glazing in cross section, with a glass pane (6) provided on each of its faces with an antireflection stack.

Figure 3 shows laminated glazing in cross section, each of the external faces of which is antireflection-treated.

Examples 1 to 10 below are modelling results and Examples 11 to 15 were actually produced. All Examples 1 to 13 relate to four-layer antireflection stacks, while Example 14 relates to a three-layer antireflection coating. The layers were all deposited conventionally by reactive magnetic-field-enhanced sputtering in an oxidizing atmosphere using an Si or metal target to make the SiO_2 or metal oxide layers, using an Si or metal target in a nitriding atmosphere to make the nitrides and in a mixed oxidizing/nitriding atmosphere to make the oxynitrides. The Si targets may contain a small amount of another metal, especially Zr, Al, especially so as to make them more conducting.

EXAMPLES 1 to 10

For Examples 2-4 and 7 to 10a, the antireflection stack used was the following:

(6): Glass
(1): SnO_2 index $n_1 = 2$
(2): SiO_2 index $n_2 = 1.46$
(3): SnO_2 (or Si_3N_4) index $n_3 = 2$
(4): SiO_2 index $n_4 = 1.46$.

For Comparative Examples 5-6, the antireflection stack used was the following:

(6): Glass
(1): SnO_2 index = 2
(2): SiO_2 index = 1.46
(3): TiO_2 index = 2.40
(4): SiO_2 index = 1.46.

Examples 1 to 7 relate to monolithic glazing and Examples 8 to 10a relate to laminated glazing.

Example 1 (comparative)

This is the glass pane 6 in Figure 1, but without any coating. The glass is a clear silica-soda-lime glass 2 mm in thickness, sold under the name Planilux by Saint-Gobain Vitrage.

Example 2

This is the glass pane 6 in Figure 1 provided on only one face with the antireflection stack.

The table below gives the index n_i and the geometrical thickness e_i in nanometers for each of the layers:

EXAMPLE 2	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	2.0	1.46	2.0	1.46
e_i	15 nm	35 nm	90 nm	105 nm

The purpose of this example is to minimize as far as possible the R_L value of the glass pane 6 (on the coated side) at an angle of incidence of 60°.

Example 3

This is the same glazing configuration as in Example 2, but the purpose being both to reduce the R_L value on the side where the layers are and to obtain a colour in the blue-greens (negative a* and b*) in reflection, again at 60° incidence. The thicknesses have been adjusted differently:

EXAMPLE 3	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	2.0	1.46	2.0	1.46
e_i	19 nm	17 nm	100 nm	95 nm

Example 4

Again we have the configuration of Examples 2 and 3, but here the motivation is to obtain the best possible compromise between the maximum reduction in R_L at oblique incidence (60°) and the reduction in R_L at normal incidence (0°):

EXAMPLE 4	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	2.0	1.46	2.0	1.46
e_i	20 nm	35 nm	80 nm	105 nm

Comparative Example 5

This example uses a layer 3 (TiO_2) having a significantly higher index than that recommended in the invention. The optical thickness of this layer 3 is chosen to be identical to that of the layer 3 of Example 2.

EXAMPLE 5	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	2.0	1.46	2.40	1.46
e_i	15 nm	35 nm	75 nm	105 nm

Comparative Example 6

This example repeats the same sequence of layers as in Comparative Example 5, with the objective

of minimizing the R_L value on the multilayer side at oblique incidence (60°).

EXAMPLE 6	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	2.0	1.46	2.40	1.46
e_i	25 nm	35 nm	110 nm	105 nm

Example 7

This example has the configuration of Figure 2, namely a glass pane (6) coated on both its faces with the same antireflection stack A. The glass pane (6) is again made of clear Planilux glass 2 mm in thickness.

The objective here is to obtain a good compromise between reducing R_L and obtaining an attractive colour in reflection, again at 60°.

EXAMPLE 7	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	2.0	1.46	2.0	1.46
e_i	19 nm	17 nm	100 nm	95 nm

Comparative Example 8

This is laminated glazing as shown in Figure 3, but without any antireflection coating.

Its structure is as follows:

➔ glass pane 6: glass bulk-tinted in the greens, having the reference TSA^{3+} from Saint-Gobain Vitrage, and having the characteristics described in Patent EP 0 644 164 (the composition is very similar to that described in the last example of the said patent, but with a total iron content expressed in the form of Fe_2O_3 which is only 0.92% by weight) and a thickness of 2.1 mm;

➔ sheet 7: 0.7 mm PVB sheet;

➔ glass pane 6': clear Planilux glass 1.6 mm in thickness.

Example 9

This is the laminated glazing in Figure 3, with the structure described in Comparative Example 8 and on the 4 face (conventionally, the faces of the glass panes making up glazing are numbered in ascending order increasing from the outside to the inside of the passenger compartment or the building in which the glazing is to be fitted), only a single antireflection stack according to the invention, the characteristics of which are given below: the objective here is to achieve the best compromise between reducing R_L and obtaining a satisfactory colour in reflection on the "layers side" at oblique incidence (60°):

EXAMPLE 9	**LAYER (1)**	**LAYER (2)**	**LAYER (3)**	**LAYER (4)**
n_i	2.0	1.46	2.0	1.46
e_i	19 nm	17 nm	100 nm	95 nm

Example 9a

This is the same glazing as in Example 9, except that here the glass pane 6 is thicker, having a thickness of 3.3 mm, so as to achieve a greater filtering effect with respect to solar radiation.

Example 10

This is the laminated structure shown in Figure 3 and Example 8, with, on the 4 face, the stack A according to Example 9 and, on the 1 face, an antireflection coating 3 different from A and consisting of a layer of SiO_xN_y whose refractive index decreases through its thickness in accordance with the teaching of the aforementioned patent FR98/16118 and which may be deposited by plasma CVD. Its thickness is about 260 nm.

Example 10a

This is the same glazing as in Example 9, except that here the glass pane 6 is thicker, having a

thickness of 4.00 mm, in order to achieve a greater filtering effect with respect to solar radiation.

EXAMPLES 11 to 13

All these examples were actually produced on clear glass panes 6 of the Planilux type with a thickness of 2 mm in the case of Examples 11 and 12 and a thickness of 4 mm in the case of Example 13.

Example 11

The glass pane in accordance with Figure 1 was coated, on one of its faces only, with the following antireflection stack according to the invention:

$Glass^{(6)}/SnO_2{}^{(1)}/SiO_2{}^{(2)}/SnO_2{}^{(3)}/SiO_2{}^{(4)}$

EXAMPLE 11	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	≈2.05	≈1.46	≈2.05	≈1.46
e_i	19 nm	17 nm	100 nm	95 nm

The SiO_2 layers contain in fact about 10% by weight of aluminium oxide so as to give them better durability, especially chemical durability.

The aim of this example is to lower the R_L at 60° and to obtain negative values of a* and b* in reflection and for these to be, in absolute values, not very high in oblique reflection (again on the layers side).

Example 12

Compared with Example 11, the two SnO_2 layers have been substituted with two Si_3N_4 layers.

The sequence is therefore the following:

$Glass^{(6)}/Si_3N_4{}^{(1)}/SiO_2{}^{(2)}/Si_3N_4{}^{(3)}/SiO_2{}^{(4)}$

EXAMPLE 12	LAYER (1)	LAYER (2)	LAYER (3)	LAYER (4)
n_i	≈2.08	≈1.46	≈2.08	≈1.46
e_i	19 nm	17 nm	100 nm	95 nm

The SiO_2 layers also contain about 10% aluminium oxide by weight.

Substituting Si_3N_4 for SnO_2 makes it possible for the stack to be bendable/toughenable. This means, within the context of the invention, that when the coated substrate undergoes a heat treatment of this type, its optical properties remain almost unchanged. Quantitatively, it may be estimated that there is no significant optical change in reflection when the value of $\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$, which measures the variations in L*, a* and b* before and after heat treatment, remains less than 2.5 or better still, less than 2.

Example 13

The glazing according to this example is treated on both its faces. It is provided both on the 1 face and on the 2 face with the same stack, that used in Example 11 (alternatively, one or both of the SnO_2 layers may be replaced with Si_3N_4).

The table below gives for all the examples of the present patent the following photometric values:

- $R_L(60°)$: the light reflection on the "layers side" at 60° with respect to the normal to the glazing, under illuminant D_{65}, in %;
- a*(60°), b*(60°): the dimensionless colorimetric values of $R_L(60°)$;
- $R_L(0°)$: the light reflection on the "layers side" at normal incidence, in %;
- a*(0°), b*(0°): the dimensionless colorimetric values of R_L at normal incidence;
- $T_L(0°)$: the light transmission under illuminant D_{65}, in %.

EXAMPLE	R_L(60°)	a*(60°)	b*(60°)	R_L(0°)	a*(0°)	b*(0°)	T_L(0°)
1	15.4	-0.3	-0.3	8.0	-0.2	-0.5	90.8
2	11.8	2.2	-4.5	5.8	3.5	-19.3	92.9
3	12.1	-1.0	-1.9	5.3	-2.2	-2.6	93.5
4	11.9	1.8	-1.9	5.0	9.8	-23.5	93.8
5	13.8	5.4	-4.3	9.1	1.2	-17.3	89.7
6	11.8	2.1	-4.8	6.2	-5.6	-6.6	92.5
7	7.9	-2.9	-6.3	2.5	-7.0	-7.0	96.3
8	13.7	-2.9	0.4	7.2	-2.8	0.0	78.7
9	10.0	-5.6	-1.2	4.5	-6.1	-1.9	80.7
9a	9.1	-6.8	-1.6	4.0	-7.3	-2.0	75.0
10	7.3	-3.3	-2.9	1.8	-5.6	-6.0	83.4
10a	6.5	-4.8	-3.2	1.7	-6.2	-5.7	75.0
11	11.8	-0.7	-0.8	5.3	-3.4	-0.4	92.3
12	11.6	-0.6	-0.9	5.2	-3.7	-7.1	94.0
13	7.7	-0.6	-2.1	2.3	-3.7	-7.1	95.3

Examples 11 and 12 underwent a mechanical durability test, the TABER test consisting in subjecting the substrate on its face coated with the thin layers to a circular rubbing action by abrasive grinding mills with a load of 500 grams. After 650 revolutions, the observed difference in haze ΔH was 1.6 in the case of Example 12 and only 0.5 in the case of Example 13.

This confirms that the stacks according to the invention, even when deposited by sputtering, have a satisfactory durability which is further enhanced if preference is given to Si_3N_4 rather than to SnO_2 for making all or some of the high-index layers.

From the summarizing table of the photometric data for all of the examples, it is possible to make the following comments:

➔ once the refracted indices have been selected, the geometrical thicknesses of the layers may be adjusted according to whether the R_L or the colorimetric response is emphasized: comparing Examples 2 and 3, it may be seen that the R_L at 60° may go below the 12%

level, but with a positive a*(Example 2), for a clear glass substrate coated especially on only one face, or else to have a slightly higher R_L value but offset by being certain of having a* and b* values at 60° which are more negative;

➔ Example 4 allows both the R_L at 60° to go below the 12% level and the R_L at 0° to reach 5%. This may be beneficial when the application is for glass of the counter type, which is liable to be observed at very varied angles of incidence;

According to the invention, R_L at oblique incidence may go below 8% if the glass is provided with antireflection stacks on both its faces (Example 7);

➔ Comparative Examples 5 and 6 show the advantage of using SnO_2 or Si_3N_4 rather than TiO_2 as the high-index layer: Example 5 tries to reproduce, in optical thickness, Example 2 (the optical thickness of layer 3 is 180 nm in both cases), but the result is less good: the R_L at 60° is 13.8%. Example 6 shows that better R_L values at 60° may be achieved, but at the expense of greatly thickening the layer 3 (optical thickness of 264 nm), which is not satisfactory in terms of production efficiency;

➔ The examples of laminated glazing confirm the benefit of providing car windscreens with antireflection coatings according to the invention;

➔ A reduction of more than 6% in R_L at 60° is achieved for a windscreen treated on both faces with the stack of the invention deposited on the 4 face (Example 10) as compared with a standard windscreen (Example 8). This therefore makes it possible either to increase the level of light transmission or to use darker or thicker glass, and therefore to provide better heat protection for the passengers in the vehicle, while still exceeding the 75% level for T_L; this is shown by Examples 10 and 10a on the one hand, and Examples 9 and 9a on the other;

➔ Examples 11 to 13 confirm the modelled results: as compared with the bare glass of Example 1, the R_L at

60° is thus reduced by at least 3%, almost 4%, while managing to keep the corresponding a* and b* values negative and, in absolute value, at most 2.1 (and even at most 1 in absolute value in the case of a*). The effect is even more pronounced if the glass is treated on both its faces, when there is a drop of more than 7% in the R_L at 60°. Furthermore, in all cases, there is also an appreciable reduction in the R_L at normal incidence (about 3% per treated face), again with negative a* and b* values: a person viewing the glazing over a wide range of angles of incidence will therefore see glazing which reflects little and does not "switch" from one colour to the other in reflection depending on the way in which he looks at it, this being highly advantageous.

Example 14

This example relates to a stack according to the invention having only three layers, the first two layers 1, 2 being replaced with a single layer 5, as shown in Figure 1.

The substrate is a clear Planilux glass 2 mm in thickness, treated on only one of its faces. The stack is as follows:

Glass/60 nm SiO_xN_y(n = 1.70)/100 nm Si_3N_4/95 nm, SiO_2.

The photometric data of the coated glass are as follows:

$R_L(60°)$ = 12.1% a* = -0.3 b* = -1.2;

$R_L(0°)$ = 5.3 % a* = -2.9 b* = -5.0;

$T_L(0°)$ = 93.5%.

It is thus possible to achieve with three layers similar performance to that of a four-layer antireflection stack according to the invention: the colorimetric response in reflection at 60° and 0° is satisfactory. The durability, especially mechanical durability, of the three-layer stack is moreover at least equivalent, if not better, than that of the four-layer stack of the invention using at least one Si_3N_4 layer.

Example 15

This example relates to laminated glazing with the ($Si_3N_4/SiO_2/Si_3N_4/SiO_2$) antireflection stack according to the invention on the 4 face and, between the two joining PVB sheets, a PET sheet functionalized by the (indium oxide/Ag/indium oxide/Ag/indium oxide) solar-protection coating.

The sequence is as follows:

Planilux glass (2.1 mm)/PVB (380 microns)/PET (160 microns)/In_2O_3 (20 nm)/Ag (7 nm)/In_2O_3 (60 nm)/Ag (7 nm)/In_2O_3 (20 nm)/PVB (380 microns)/Planilux glass (2.1 mm)/Si_3N_4 (17 nm)/SiO_2 (18 nm)/Si_3N_4 (104 nm)/SiO_2 (108 nm).

The value of the light reflection at 60°, R_L (60°), is 11.2%, whereas it is 14.9% if it is measured on laminated glazing which is identical but does not have the antireflection coating on the 4 face.

The value of T_L at 0° is 75.1% (it is 75.3% without the antireflection coating).

The value of the energy reflection at 0° (normal incidence), R_E (0°), is 25.6% and the energy transmission value at 0°, T_E (0°), is 52.2%.

This example shows the effectiveness of a solar-protection coating which significantly reflects the infrared. However, against this, the use of such a coating tends to increase the light reflection on the interior side. The antireflection stack according to the invention makes it possible to compensate for this increase in reflection and to maintain the level of reflection (on the inside) that the laminated glazing would have without the solar-protection coating.

The same solar-protection effect is obtained if a coating comprising two silver layers, deposited directly on one of the glass panes, with a single intermediate PVB sheet, is used.

CLAIMS

1. Transparent substrate (6), especially made of glass, comprising, on at least one of its faces, an antireflection coating, especially having an antireflection effect at oblique incidence, made of a stack (A) of thin layers of dielectric material having alternately high and low refractive indices, **characterized in that** the stack comprises, in succession:

- a high-index first layer (1), having a refractive index n_1 of between 1.8 and 2.2 and a geometrical thickness e_1 of between 5 and 50 nm;
- a low-index second layer (2), having a refractive index n_2 of between 1.35 and 1.65 and a geometrical thickness e_2 of between 5 and 50 nm;
- a high-index third layer (3), having a refractive index n_3 of between 1.8 and 2.2 and a geometrical thickness e_3 of between 70 and 120 nm;
- a low-index fourth layer (4), having a refractive index n_4 of between 1.35 and 1.65 and a geometrical thickness e_4 of at least 80 nm.

2. Substrate (6) according to Claim 1, **characterized in that** n_1 and/or n_3 are between 1.85 and 2.15, especially between 1.90 and 2.10.

3. Substrate (6) according to either of the preceding claims, **characterized in that** n_2 and/or n_4 are between 1.35 and 1.55.

4. Substrate (6) according to one of the preceding claims, **characterized in that** e_1 is between 5 and 50 nm, especially between 10 and 30 nm or between 15 and 25 nm.

5. Substrate (6) according to one of the preceding claims, **characterized in that** e_2 is between 5 and 50 nm, especially between 10 and 35 nm and preferably less than or equal to 30 nm.

6. Substrate (6) according to one of the preceding claims, **characterized in that** e_3 is less than or equal to 120 nm and especially at least 75 Nm.

7. Substrate (6) according to one of the preceding claims, **characterized in that** e_4 is greater than or equal to 80 nm and especially less than or equal to 120 nm.

8. Substrate (6) according to one of the preceding claims, **characterized in that** the high-index first layer (1) and the low-index second layer (2) are replaced with a single layer (5) having an intermediate index e_5 of between 1.65 and 1.80 and preferably having an optical thickness e_{opt5} of between 50 and 140 nm, preferably between 85 and 120 nm.

9. Substrate (6) according to Claim 8, **characterized in that** the intermediate-index layer (5) is based on a mixture, on the one hand, of silicon oxide and, on the other hand, at least one metal oxide chosen from tin oxide, zinc oxide and titanium oxide, or is based on a silicon oxynitride or oxycarbide and/or on aluminium oxynitride.

10. Substrate (6) according to one of the preceding claims, **characterized in that** the high-index first layer (1) and/or the high-index third layer (3) are based on one or more metal oxides chosen from zinc oxide, tin oxide and zirconium oxide or based on one or more nitrides chosen from silicon nitride and aluminium nitride.

11. Substrate (6) according to one of the preceding claims, **characterized in that** the high-index first layer (1) and/or the high-index third layer (3) consist of a superposition of several high-index layers, especially a superposition of two layers such as SnO_2/Si_3N_4 or Si_3N_4/SnO_2.

12. Substrate (6) according to one of the preceding claims, **characterized in that** the low-index second layer (2) and/or the low-index fourth layer (4) are based on silicon oxide, silicon oxynitride and/or oxycarbide or on a mixed silicon aluminium oxide.

13. Substrate (6) according to one of the preceding claims, **characterized in that** the said substrate is made of clear or bulk-tinted glass.

14. Substrate according to one of the preceding claims, **characterized in that** its light reflection on the side where the stack (A) of thin layers is provided is reduced by a minimum value of 3 or 4% at an angle of incidence of between 50° and 70°.

15. Substrate according to one of the preceding claims, **characterized in that** the colorimetric response of its light reflection on the side where the stack (A) of thin layers is provided is such that the corresponding a* and b* values in the (L*, a*, b*) colorimetry system are negative at an angle of incidence of between 50° and 70°.

16. Substrate according to one of the preceding claims, **characterized in that** the antireflection stack (A) uses, at least for its high-index third layer, silicon nitride or aluminium nitride so that it is able to undergo a heat treatment of the bending, toughening or annealing type.

17. Glazing according to one of the preceding claims, **characterized in that** it is composed of the single substrate (6) provided, on one of its faces, with the multilayer antireflection stack (A) and, on its other face, either with no antireflection stack or also with a multilayer antireflection stack (A), or with another type (B) of antireflection coating, or with a coating having another functionality of the solar-protection, low-emissivity, antifouling, antifogging, anti-rain or heating type.

18. Glazing according to one of Claims 1 to 16, **characterized in that** it has a laminated structure in which two glass substrates (6, 6') are joined together using a sheet (7) of thermoplastic, the substrate (6) being provided, on the opposite side to the join, with the antireflection stack (A) and the substrate (6') being provided, on the opposite side to the join, either with no antireflection coating, or also with an antireflection stack (A), or with another type (B) of antireflection coating, or with a coating having another functionality of the solar-protection,

low-emissivity, antifouling, antifogging, anti-rain or heating type, the said coating having another functionality possibly also being on one of the faces of the substrates which are turned towards the thermoplastic joining sheet.

19. Glazing according to one of Claims 1 to 16, **characterized in that** it has a laminated structure with one or more sheets of joining polymer, with the antireflection coating (A) on the 1 and/or 4 faces and, in contact with the joining sheet or one of the joining sheets, a solar-protection coating, especially one consisting of two silver layers.

20. Glazing according to Claim 17 or Claim 18, **characterized in that** the other type (B) of antireflection coating is chosen from the following coatings:

➔ a single low-index layer, having an index of less than 1.60 or 1.50, especially about 1.35-1.48, especially based on silicon oxide;

➔ a single layer whose refractive index varies through its thickness, especially of the silicon oxynitride SiO_xN_y type, where x and y vary through its thickness;

➔ a two-layer stack, comprising, in succession, a layer having a high index of at least 1.8, especially made of tin oxide, zinc oxide, zirconium oxide, titanium oxide, silicon nitride or aluminium nitride, and then a layer having a low index, of less than 1.65, especially made of silicon oxide, oxynitride or oxycarbide;

➔ A three-layer stack comprising, in succession, a layer having a medium index of between 1.65 and 1.8 of the silicon oxycarbide or oxynitride and/or aluminium oxycarbide or oxynitride type, a layer having a high index of greater than 1.9 of the SnO_2 or TiO_2 type, and a layer having a low index of less than 1.65, of the mixed Si-Al oxide or silicon oxide type.

21. Process for obtaining the glazing according to one of Claims 17; 18 or 20, **characterized in that** the

antireflection stack or stacks (A) is/are deposited by sputtering and the optional antireflection coating (B) is deposited by a sol-gel technique, by a pyrolysis technique of the CVD or plasma CVD type, by sputtering or by corona discharge.

22. Application of the glazing according to one of Claims 17 to 20 as interior or exterior glazing for buildings, as a shop display cabinet or counter, which may be curved, as glazing for vehicles, such as the side windows, the rear window, the sunroof and the windscreen, or as glazing for protecting objects of the painting type, or as an antidazzle computer screen, or as glass furniture.

TRANSPARENT SUBSTRATE COMPRISING AN ANTIREFLECTION COATING

ABSTRACT

The subject of the invention is a transparent substrate (6), comprising an antireflection coating, made from a stack (A) of thin layers of dielectric material having alternately high and low refractive indices. This stack comprises:

- a high-index first layer (1), having a refractive index n_1 of between 1.8 and 2.2 and a geometrical thickness e_1 of between 5 and 50 nm;
- a low-index second layer (2), having a refractive index n_2 of between 1.35 and 1.65 and a geometrical thickness e_2 of between 5 and 50 nm;
- a high-index third layer (3), having a refractive index n_3 of between 1.8 and 2.2 and a geometrical thickness e_3 of between 70 and 120 nm;
- a low-index fourth layer (4), having a refractive index n_4 of between 1.35 and 1.65 and a geometrical thickness e_4 of at least 80 nm.

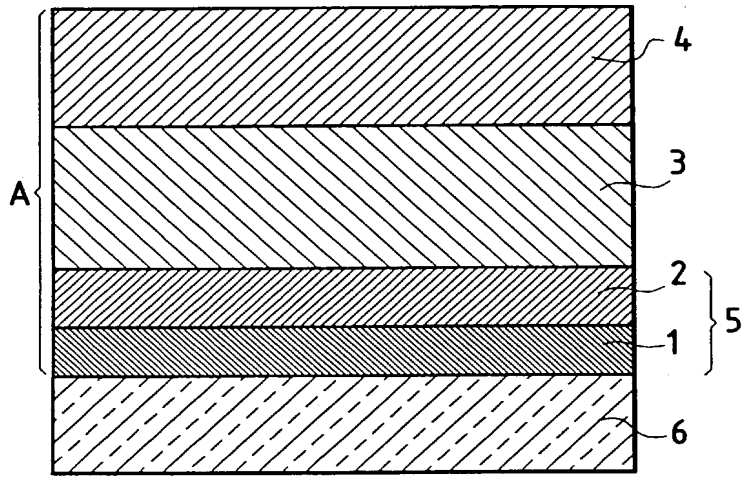

FIG.1

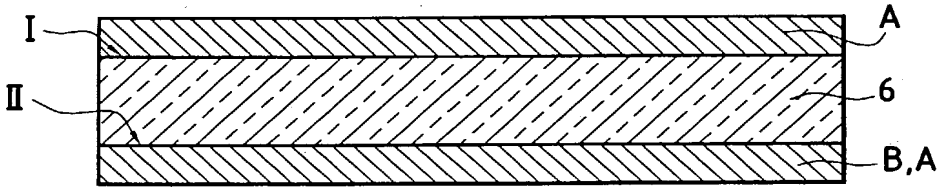

FIG.2

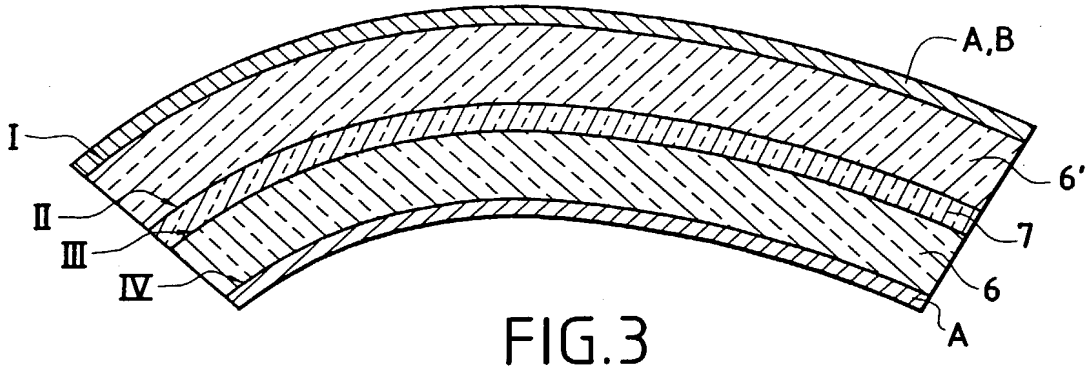

FIG.3

Docket No. 219924US2PCT

Declaration and Power of Attorney for Patent Application
Déclaration et Pouvoirs pour Demande de Brevet

French Language Declaration

En tant l'inventeur nommé ci-après, je déclare par le présent acte que:

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

et dont la description est fournie ci-joint à moins

☐ ci-joint

☐ a été déposée le _____

sous le numéro de demande des Etats-Unis ou le numéro de demande international PCT

_____ et modifiée le

_____ (le cas échéant).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

As a below named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

TRANSPARENT SUBSTRATE COMPRISING AN ANTIREFLECTION COATING

the specification of which

☐ is attached hereto.

☒ was filed on November 17, 2000

as United States Application Number or PCT International Application Number

PCT/FR00/03209 and was amended on

_____ (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

French Language Declaration

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

I hereby claim foreign priority under Title 35, United States Code, § 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)
Demande(s) de brevet anterieure(s) dans un autre pays.

(Number) (Numéro)	(Country) (Pays)	(Day/Month/Year Filed) (Jour/Mois/Anné de dépôt)	Priority Claimed Droit de priorité Revendiqué Yes / Oui	 No / Non
99 14423	France	17 November 1999	☒	☐

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 119(e) du Code des Etats-Unis, de toute demande de brevet provisoire effectuée aux Etats-Unis et figurant ci-dessous.

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

(Application No.) (Nº de demande)	(Filing Date) (Date de dépôt)	(Application No.) (Nº de demande)	(Filing Date) (Date de dépôt)

Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande:

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application No.) (Nº de demande)	(Filing Date) (Date de dépôt)	(Status: Patented, Pending, Abandoned) (Statut : breveté, en cours d'examen, abandonné)
PCT/FR00/03209	November 17, 2000	

Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d' une incarcération, ou des deux, en vertu de la § 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

French Language Declaration

POUVOIRS: En tant que l'inventeur cité, je désigne par la présente l'(les) avocat(s) suivant(s) pour qu'ils poursuive(nt) la procédure de cette demande de brevet et traite(nt) toute affaire s'y rapportant avec l'Office des brevets et des marquees: *(mentionner le nom et le numéro d'enregistrement).*

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

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French Language Declaration

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Signature de l'inventeur Date	Fourth inventor's signature Date 7.4.02
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Nationalité	Citizenship Germany
Adresse Postale	Mailing Address Same as above

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Signature de l'inventeur Date	Fifth inventor's signature Date 18/05/2002
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Nationalité	Citizenship Germany
Adresse Postale	Mailing Address Same as above